

Reactivity of Haloethanes with Hydroxyl Radicals: Effects of Basis Set and Correlation Energy on Reaction Energetics

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ABSTRACT: *Ab initio* calculations on fluoroethane reactions with the hydroxyl radical have been carried out at different levels of theory. The convergence of reaction barriers and reaction enthalpies has been systematically investigated with respect to the size and quality of the basis set and the treatment of correlation energy. The G2 and MP2 barrier heights and reaction enthalpies show the best agreement with the experimental data. The split valence basis sets of triple-zeta quality supplemented by diffuse and polarization functions are necessary to reproduce experimental values for barrier heights and reaction enthalpies at the MP2 level of theory. The full counterpoise correction was used to calculate the basis set superposition error for several standard basis sets, including polarization and diffuse functions. The smallest counterpoise corrections are associated with basis sets that contain polarization and diffuse functions, the diffuse functions being the most effective in reducing BSSE. However, in our case, the uncorrected barrier heights are in better agreement with experimental results than the counterpoise-corrected data. Thus, at the MP2 level of theory, which seems to be dictated for larger electronic systems of chemical interest, the optimal approach is to increase the basis set to the maximum size affordable and to use results without counterpoise corrections for the calculation of reaction barriers. A viable alternative is the use of G2 theory because its results for the barrier heights and reaction enthalpies are in excellent agreement with the experimental data. © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 1190–1199, 1997

Keywords: *ab initio* calculations; basis set superposition error; correlation energy; halogenated alkanes; hydrogen abstraction by hydroxyl radical; reaction barriers and reaction enthalpies

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Introduction

A*b initio* calculations on weakly bound systems, that is, supermolecular complexes such as van der Waals complexes, transition-state structures, and similar systems, are now routinely performed¹ with the objective to obtain results whose quality will approach the “chemical accuracy” (ca. 1 kcal mol⁻¹). However, at the same time, accurate predictions of interaction energies by *ab initio* methods are influenced by the application of a limited basis set and the incomplete treatment of correlation energy.^{1,2} In addition, truncation of a basis set for supermolecular complexes results in a phenomenon known as basis set superposition error (BSSE). This study is a systematic analysis of the influence of the basis set quality, electron correlation, and BSSE on the reaction barrier height and the reaction enthalpy of hydrogen abstraction reactions; that is, hydroxyl (OH) radical reaction with fluoro- and chloroethane. It must be emphasized that the objective of this work is to provide a better understanding, classification, and evaluation of the quality and efficiency of the most popular computational approaches in determining the reaction barrier height and the reaction enthalpy due to our plans to extend this study to larger electronic systems, which are of interest in atmospheric chemistry.

The problem of BSSE was recognized almost 30 years ago.³ Since then many articles have been published on this subject, including comprehensive reviews by van Lenthe et al.,⁴ Scheiner,⁵ and Chalasinski and Szczesniak.¹ Use of large basis sets should minimize BSSE, but for the majority of electronic systems of chemical interest smaller basis sets are dictated. Even for moderate-sized basis sets, basis set superposition error can be significant.^{6,7} Furthermore, it was found⁷⁻¹⁰ that BSSE does not behave monotonically, but initially increases with the size of the basis set, and after passing through maximum decreases as the basis set becomes larger. Thus, the discussion concerning the necessity of accounting for and methodologies to treat BSSE are still numerous and ongoing.^{1,5} The majority of studies favor the full counterpoise correction of Boys and Bernardi.¹¹ However, its application does not guarantee that the “exact result” will be obtained and several studies have been published recently in which the adequacy of the counterpoise procedure is re-

evaluated.^{8,12} Recently, attempts have been made to derive approaches that will eliminate the BSSE effects *a priori*, at the stage of supermolecular calculations. Examples include the “chemical Hamiltonian approach,”¹²ⁱ the “strictly monomer molecular orbital” SCF approach,^{12j} and the “constrained dimer function” approach.^{12k}

The effect of the BSSE upon the energetics of the formation of the van der Waals complexes has been studied extensively and results are reported in the literature. Unfortunately, little is known about how this error affects the potential energy surface in a chemical reaction; that is, the formation of transition-state structures and the corresponding barrier heights. To our knowledge, the recent publication by Scheiner and colleagues¹³ on proton transfer is one of the first efforts in this area. Thus, in this study, the contribution of the BSSE and its effect on the calculated activation energies of the hydrogen abstraction reactions is systematically studied with respect to the size of the basis set as well as the treatment of electron correlation. Typically, the magnitude of the BSSE at correlated levels is more severe than at the SCF level.^{4,5}

Another problem that may affect the quality of *ab initio* calculations is the inadequate description of correlation energy, which dominates the interaction energy between reactant units in the transition-state complex. The Møller–Plesset perturbation theory is widely used as an efficient dynamic correlation correction beyond the Hartree–Fock level, because it provides a size-consistent description of electron correlation effects.¹⁴ However, it was found, in some cases, that its convergence may be slow, and that the third and the fourth order Møller–Plesset contributions almost cancel each other.^{1,15,16} However, this does not seem to be true in general.¹ It is also known that accuracy of any correlated electronic structure calculation can be highly dependent on the one-particle basis set used to represent the molecular orbitals.^{1,17} Thus, the performance of the Møller–Plesset perturbation method (including second, third, and fourth order terms) is systematically investigated in calculations of barrier heights and reaction enthalpies for fluoroethane and chloroethane reactions with the hydroxyl radical using different basis sets. Our study was not extended to the higher levels of theory such as coupled cluster [CCSD or CCSD(T)] and configuration interaction [QCISD(T)] methods because they are computationally too demanding to be applied to large electronic systems, which are of interest in atmo-

spheric chemistry; that is, C_2 to C_4 alkanes substituted with three or more halogen atoms. The primary reason for reporting and analyzing the results of the "low level calculations," that is, MP2/6-31G(d,p) or similar, is that this level of theory is dictated for larger electronic systems of chemical interest. Because this situation will not change dramatically in the future, it is important to evaluate also the quality and efficiency of the "low level calculations."

The reaction with hydroxyl radical is the primary loss channel for the partially halogenated hydrocarbons in the troposphere,¹⁸ which proceeds by the abstraction of the hydrogen atom. Two pathways (R1 and R2) are feasible for reactions of fluoroethane^{19,20} and chloroethane²¹ with the hydroxyl radical; that is, the abstraction of hydrogen from α and β carbon atoms:



Recently, it was found that reaction R2 has two possible pathways (R2a and R2b), via two rotamer transition-state structures.^{19–21} Both rotamers are first-order saddle points. The geometry of one rotamer resembles, to a large extent, the transition-state structure of an α -abstraction reaction.^{19–21} The other rotamer, obtained by the rotation around the reactive C—H bond, is stabilized by a through-space interaction, which lowers the barrier height for the β abstraction by 1.45 and 0.96 kcal mol⁻¹ for fluoroethane^{19,20} and chloroethane,²¹ respectively. This interaction is due mainly to the delocalization of electrons from the halogen nonbonding orbital into the antibond orbital of the OH radical.^{20,21}

The reaction barrier heights [$E_0^{(298K)}$] and the reaction enthalpies [$\Delta H_r^{(298K)}$] have been calculated for all possible reaction pathways of fluoroethane and chloroethane reactions with the hydroxyl radical using the range of commonly used split valence basis sets of increasing size from 6-31G(d,p) to 6-311+G(3df,2p). In addition, the Dunning correlation-consistent basis set, cc-pVTZ,²² was also tested. Correlation was included at the second, third, and fourth order of Møller–Plesset perturbation theory. The full counterpoise correction (CP), proposed by Boys and Bernardi,¹¹ was used to estimate BSSE at the SCF and all correlated levels. Furthermore, the reaction barrier heights and the reaction enthalpies are also deter-

mined at the G2 level of theory.²³ The quality of the calculated results was evaluated by comparison with the available experimental data.^{20,21,24} Experimental barrier heights were obtained^{20,21,24} from the temperature dependence of the reaction rate constants following the Arrhenius or modified Arrhenius equations. The evaluation was also performed by comparison of the calculated data with the G2 values, because it was shown²⁰ that this approach can reproduce the experimental reaction barrier heights and reaction enthalpies for hydrogen abstraction with an accuracy of 1 kcal mol⁻¹.

Methods

All calculations were carried out using the GAUSSIAN 92 program package²⁵ running on a SiliconGraphics Iris Indigo R4000 workstation equipped with a 2-GB hard disk and 48 MB of RAM memory. Pople-type split valence basis sets,^{14,26} from 6-31G(d,p) to 6-311+G(3df,2p), with the standard exponents for polarization and diffuse functions and Dunning's cc-pVTZ basis set²² have been employed in this study. The electron correlation correction was carried out by the application of the Møller–Plesset perturbational approach at the second (MP2), third (MP3), and fourth order (MP4) of theory.^{27,28} Calculations were performed for closed-shell as well as for open-shell systems. The annihilation of the spin contaminants from the unrestricted wave functions is mandatory to obtain reliable results.^{29,30} Thus, Schlegel's spin projection scheme³⁰ was used for the open-shell systems to eliminate the spin contamination arising from the states with spin $s + 1$ to $s + 4$. In the remaining part of this study, the abbreviation "U" will be omitted in descriptions of calculations with the unrestricted wave functions. Thus, the identical acronyms, HF and MPn, will be used for the calculations performed on closed-shell and open-shell systems. PMP2, PMP3, and PMP4 will describe results where the spin projection was applied.

The total energies for all species were determined using GAUSSIAN-2 (G2) theory.²³ Two modifications to the original G2 theory were used: frequencies were calculated at the correlated second order Møller–Plesset level, and the originally proposed 6-31G(d) basis set was supplemented with the polarization functions on hydrogen atoms because the processes of hydrogen atom abstrac-

tion were studied. The same modifications to the G2 procedure have been used by others.¹⁹

All calculated energies were corrected for the zero-point and thermal energies to compare them with experimental results. The unscaled vibrational frequencies were used for calculating the zero-point and thermal energy corrections.

Basis set superposition error (BSSE) was calculated by the full function counterpoise correction (CP) proposed by Boys and Bernardi.¹¹ With the CP approach, the same basis sets are applied to the energy calculations of isolated molecules (reactants) and for the supermolecule (transition-state structure). The magnitude of the BSSE can then be estimated from eq. (1):

$$\begin{aligned} \text{BSSE} &= \Delta E_{\text{AB}}^{\text{CP}} - \Delta E_{\text{AB}} \\ &= [E(\text{A}) - E(\text{AG}_{\text{B}})] + [E(\text{B}) - E(\text{BG}_{\text{A}})] \end{aligned} \quad (1)$$

where $\Delta E_{\text{AB}}^{\text{CP}}$ and ΔE_{AB} are the potential energies obtained with and without the CP correction for the intermolecular system AB, and $E(\text{A})$, $E(\text{B})$, $E(\text{AG}_{\text{B}})$, and $E(\text{BG}_{\text{A}})$ are the system energies for the monomers A and B without and with the CP method. The $E(\text{AG}_{\text{B}})$ is obtained from a calculation that includes not only its own basis functions but also a set of functions that are located at reactant B. The functions on B are then called ghost functions.

The convergence of Møller–Plesset perturbation theory is of utmost importance for the practical calculations of the interaction energies. The interaction energy (ΔE^{tot}) is composed of two parts, the Hartree–Fock energy contribution (ΔH^{HF}) and the correlation energy corrections (ΔE^{corr}):

$$\Delta E^{\text{tot}} = \Delta H^{\text{HF}} + \Delta E^{\text{corr}} \quad (2)$$

The ΔE^{corr} terms at the MP2, MP3, and MP4 levels of theory can be expressed by eqs. (3), (4), and (5), respectively. $\Delta E^{(2)}$, $\Delta E^{(3)}$, and $\Delta E^{(4)}$ are the correlation energy terms calculated at the second, third, and fourth order of Møller–Plesset perturbation theory, respectively:

$$\Delta E^{\text{corr}}(\text{MP2}) = \Delta E^{(2)} \quad (3)$$

$$\Delta E^{\text{corr}}(\text{MP3}) = \Delta E^{(2)} + \Delta E^{(3)} \quad (4)$$

$$\Delta E^{\text{corr}}(\text{MP4}) = \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)} \quad (5)$$

Efficient perturbation expansion should recover the major portion of the interaction energy through the second-order term and provide accurate results through the fourth order term. Therefore, the con-

vergence and overall performance of the Møller–Plesset perturbational approach will be evaluated for the second (MP2), third (MP3), and fourth order (MP4) of theory. Pople’s approximation³¹ [eq. (6)] will be used to estimate the full correlation energy for all stationary points and to evaluate results obtained at different levels of Møller–Plesset perturbation theory.

$$E^{\text{corr}} = \frac{E^{(2)} + E^{(3)}}{1 - E^{(4)}/E^{(2)}} \quad (6)$$

Results and Discussion

The reaction enthalpies and barrier heights are calculated for the fluoroethane reaction with the hydroxyl radical using seven different basis sets (Table I) and the second, third, and fourth order Møller–Plesset perturbation theory. Geometries of all species are optimized and vibrational analysis is performed at the MP2/6-31G(d,p) level of theory. The detailed description of the calculated equilibrium geometries, vibrational analysis of the stationary points, as well as the comparison with the results of the ethane^{32,33} and chloroethane²¹ reactions with the hydroxyl radical have been previously reported.²⁰

BARRIER HEIGHTS

The calculated barrier heights for the α -abstraction reaction of fluoroethane are shown in Table I. They are reported as the differences between the calculated and experimental values. Thus, smaller numbers, positive or negative, indicate better agreement with the measured data. Results for the β -abstraction reaction are analogous to the results obtained for the α -abstraction reaction.^{19,20} The β -abstraction reaction proceeds via two possible pathways and both have higher barrier height than the α -abstraction reaction. It is also less exothermic than α abstraction. At room temperature the α -abstraction reaction is preferred.¹⁸ Similar trends have been observed for the abstraction reactions on chloroethane.^{20,21} Thus, our discussion will focus on results obtained for the α -abstraction reaction of fluoroethane.

The spin contamination of unrestricted wave functions for transition-state structures and radicals is small but still it has a noticeable effect on the calculated barrier heights. The largest spin contamination is obtained for the transition-state

TABLE I.
Basis Set Dependence of Calculated Barrier Heights for α -Abstraction Reaction (R1) of Fluoroethane at Second, Third, and Fourth Order Møller–Plesset Perturbation Theory with Corrections for Zero-Point and Thermal Energies.^a

Basis set	$\Delta E_0^{(\text{MP2})}$	$\Delta E_0^{(\text{PMP2})}$	$\Delta E_0^{(\text{MP3})}$	$\Delta E_0^{(\text{PMP3})}$	$\Delta E_0^{(\text{MP4})}$	$\Delta E_0^{(\text{PMP4})}$
6-31G(d, p)	3.71	1.65	6.81	5.61	3.96	2.75
6-311G(d, p)	2.71	0.60	5.67	4.42	2.19	0.94
6-311+G(d, p)	3.04	0.92	6.04	4.81	2.30	1.07
6-311+G(2d, p)	2.73	0.60	6.03	4.80	2.19	0.96
6-311G(2df, p)	1.62	−0.50	4.88	3.61	1.26	−0.01
6-311+G(3df, 2p)	1.87	−0.26				
cc-pVTZ	−0.05	−1.87				

^a Results are reported as the difference between the calculated and experimental values, in kilocalories per mole. Experimental barrier height for the hydrogen abstraction reaction in fluoroethane is 2.15 kcal mol^{−1}.²⁴

structures, but $\langle S^2 \rangle$ is never larger than 0.78. The effect of spin projection on the calculated barrier heights is shown in Table I. The projection of the spin contamination lowers the MP2, MP3, and MP4 barrier heights by about 2.1, 1.2, and 1.2 kcal mol^{−1}, respectively, and in all cases improves their agreement with the experimental data. Thus, the annihilation of the spin contaminants from the unrestricted wave functions seems mandatory for calculation of reaction barriers.

The effect of incomplete description of correlation energy on calculated barrier heights will be discussed next. For that purpose, the calculated barrier heights are divided into the Hartree–Fock and correlated contributions [eqs. (2)–(5)]. Those results are reported in Table II. As expected, the inclusion of correlation energy significantly decreases calculated reaction barriers, and the major part of correlation energy is already described by the MP2 term. The higher order contributions (MP3 and MP4) are still significant but they almost cancel each other. Similar behavior of Møller–Plesset

perturbation expansion has already been reported in several instances.^{1, 15, 16} In most cases (Table II) the fourth order terms ($\Delta E^{(4)}$) are larger than the third order terms ($\Delta E^{(3)}$). The net effect is that the MP2 and MP4 levels of theory give very similar barrier heights for the hydrogen abstraction reactions, which are in very good agreement with experimental results. The barrier heights calculated at the MP3 level of theory are significantly overestimated.

Due to the oscillatory behavior of MP3 and MP4 terms for all basis sets used (Table II), the convergence of the Møller–Plesset series was checked. The full correlation energies of stationary points have been estimated by the Pople’s approximation³¹ [eq. (6)]. It is found that the changes in reaction barriers due to the extrapolation are generally small, less than 0.33 kcal mol^{−1}. Therefore, we can conclude that barrier height values are well converged despite the fact that the correlation energies of the reactant and transition-state structures have not converged to the same level.

The barrier heights have been calculated with a several commonly used basis sets of increasing size from 6-31G(d, p) to 6-311+G(3df, 2pd), plus Dunning’s cc-pVTZ basis set, and these results are shown in Table I. The quality of results improves in general with the size of basis set but it seems that the split valence basis sets of triple-zeta (TZ) quality supplemented by diffuse and polarization functions are necessary to reproduce the experimental values for barrier heights. An unexpected result is obtained with the largest basis set employed in this study (i.e., Dunning’s cc-pVTZ basis set) at the PMP2 level of theory. The calculated barrier height underestimates the measured value by nearly 2 kcal mol^{−1}. Unfortunately, due to the

TABLE II.
Decomposition of Calculated Barrier Heights for α -Abstraction Reaction of Fluoroethane, Without Spin Projection Corrections, into Hartree–Fock and Correlated Contributions.^a

Basis set	ΔE_0^{HF}	$\Delta E_0^{(2)}$	$\Delta E_0^{(3)}$	$\Delta E_0^{(4)}$
6-31G(d, p)	22.25	−14.58	2.97	−2.86
6-311G(d, p)	21.82	−15.26	2.95	−3.48
6-311+G(d, p)	22.54	−15.66	2.99	−3.84
6-311+G(2d, p)	22.70	−16.13	3.30	−3.83
6-311G(2df, p)	21.88	−16.42	3.26	−3.62

^a Results are in kilocalories per mole.

limited computational resources, we were not able to test this large basis set augmented by diffuse functions or in combination with higher levels of perturbational approach, MP3 or MP4.

To estimate the energy lowering of transition-state structures due to the incomplete description of reactant orbital space, the full counterpoise (CP) method was employed [eq. (1)]. The basis set superposition errors (BSSEs) calculated for five Pople-type basis sets are given in Table III. The BSSE data have not been calculated for the cc-pVTZ basis set due to the SCF convergence problems coupled with limited computational facilities. The BSSE values calculated at the HF level are significantly lower than those calculated on the correlated levels, in agreement with previous findings.^{12,13} The most significant reduction (ca. 2.5 kcal mol⁻¹) of BSSE has been observed at the correlated levels for the basis sets supplemented by diffuse functions. The reason may be that the diffuse functions provide a better description of orbital space between the interacting units and, consequently, more adequate treatment of exchange interactions. The addition of polarization functions, the second or third d and one f set for fluorine, carbon, and oxygen atoms, also reduces BSSE, but the effect is smaller (ca. 1 kcal mol⁻¹). Thus, it seems that, to reduce BSSE below 1 kcal mol⁻¹, the split valence basis sets of TZ quality supplemented by diffuse and d-type and f-type polarization functions will be needed. Finally, it is of interest to note that, for each basis set employed in this study, the BSSE values are very close for all correlated levels, MP2, MP3, and MP4.

The counterpoise-uncorrected barrier heights are reported because they are in better agreement with the experimental results than the counterpoise-corrected data. A similar result was obtained in several recent, extensive and systematic studies on

hydrogen bonding in HF^{12e} and water^{12h,34} dimers. The calculated binding energies for HF and water dimers without counterpoise corrections are in better agreement with experimental binding energies at the MP2 levels of theory with the following series of correlation-consistent basis sets augmented by diffuse functions: aug-cc-pVDZ; aug-cc-pVTZ; and aug-cc-pVQZ. In all these cases counterpoise corrections reduce the quality of calculated binding energies for HF and water dimers. Thus, it seems that, in all these cases, counterpoise corrections are counterproductive. A similar conclusion was recently suggested^{12g} in the study on van der Waals complexes of helium and neon with the methane molecule, namely the MP3/6-311++G(3d,3p) without BSSE correction was selected as the appropriate level of theory for the calculation of interaction energies between helium or neon and methane. However, it should be pointed out that the CP-corrected and CP-uncorrected binding energies for the HF dimer calculated by the MP2, MP4, and coupled cluster [CCSD and CCSD(T)] methods^{12e} converge, with the increased basis set sizes, essentially to the experimental binding energy.

Another criterion for assessing the usefulness of counterpoise corrections is the spread of the calculated energies with and without corrections. If the counterpoise-corrected results for a given set of basis sets have a smaller spread than the uncorrected data, it may be concluded that the CP systematically reduces uncertainties and systematically improves the accuracy of the calculations. However, the opposite seems to be the case at the SCF and all correlated levels of theory. For example, the spread of uncorrected MP2 energies is 2.1 kcal mol⁻¹, whereas the spread of counterpoise-corrected energies is almost double, 3.9 kcal mol⁻¹.

Thus, the usefulness of counterpoise corrections seems to be questionable and it should be used with caution. Our suggestion is to increase the basis set to the maximum affordable size and to use results from calculations without counterpoise corrections.

REACTION ENTHALPY

The reaction enthalpies are calculated as the energy difference between reactants and products. The calculated reaction enthalpies, for the α -abstraction reaction of fluoroethane are shown in Table IV. They are reported as the differences between calculated and experimental³⁵ values. Thus, smaller numbers, positive or negative, indi-

TABLE III.
Basis Set Superposition Error (BSSE) Calculated by Full Counterpoise Method for Barrier Heights of α -Abstraction Reaction of Fluoroethane.^a

Basis set	HF	MP2	MP3	MP4
6-31G(d, p)	2.25	4.87	4.63	5.14
6-311G(d, p)	2.34	5.58	5.33	5.88
6-311G(2df, p)	2.24	4.45	4.06	4.52
6-311+G(d, p)	0.99	3.01	3.05	3.31
6-311+G(2d, p)	0.71	2.01	1.95	2.15
6-311+G(3df, 2p)	0.75	1.92		

^a Results are in kilocalories per mole.

TABLE IV.

Basis Set Dependence of Calculated Reaction Enthalpies for α -Abstraction Reaction (R1) of Fluoroethane at Second, Third, and Fourth Order Møller–Plesset Perturbation Theory with Corrections for Zero-Point and Thermal Energies.^a

Basis set	$\Delta H_r^{(\text{MP2})}$	$\Delta H_r^{(\text{PMP2})}$	$\Delta H_r^{(\text{MP3})}$	$\Delta H_r^{(\text{PMP3})}$	$\Delta H_r^{(\text{MP4})}$	$\Delta H_r^{(\text{PMP4})}$
6-31G(d, p)	2.22	2.11	6.98	6.87	5.94	5.83
6-311G(d, p)	1.21	1.07	6.31	6.21	4.56	4.45
6-311+G(d, p)	-1.27	-1.31	4.44	4.44	2.26	2.26
6-311+G(2d, p)	-1.52	-1.49	4.65	4.67	2.33	2.35
6-311G(2df, p)	-0.24	-0.25	5.11	5.04	3.46	3.39
6-311+G(3df, 2p)	-3.57	-3.64				
cc-pVTZ	1.01	1.04				

^a Results are reported as difference between calculated and experimental values, in kilocalories per mole. Experimental reaction enthalpy for the α -hydrogen abstraction reaction in fluoroethane is $-18.7 \text{ kcal mol}^{-1}$.^{20,35}

cate better agreement with the measured data. As for the barrier heights, our discussion will be focused on results obtained for the α -abstraction reaction of fluoroethane because observed trends are analogous for the β -abstraction reaction^{19,20} as well as for the abstraction reactions on chloroethane.^{20,21}

Spin contamination has a negligible effect on the calculated reaction enthalpies, that is, $0.05 \text{ kcal mol}^{-1}$ for larger basis sets (Table IV).

The reaction enthalpies depend significantly on the level of correlation treatment used in the calculations. Thus, the reaction enthalpies are divided into the Hartree–Fock and correlated contributions [eq. (2)–(5)] in the same way as barrier heights to evaluate the effect of an incomplete description of correlation energy on the calculated reaction enthalpies. These results are reported in Table V. The inclusion of correlation effects significantly increases reaction enthalpies and most of the correlation energy is already described by the MP2 term. However, the third and fourth order terms do not cancel each other as in the case of calculated barrier heights. The differences between the MP2 and MP4 reaction enthalpies are significant and remain nearly constant, ca. $3.6 \text{ kcal mol}^{-1}$, regardless of the size of basis set (Table V).

The reaction enthalpies calculated at the MP2 level show better agreement with the experimental data than the reaction enthalpies calculated at the MP3 and MP4 levels of theory for all basis sets used. Poor agreement with experiment obtained at the higher levels of Møller–Plesset perturbation theory may be a result of slow convergence of the MP series. Pople's approximation [eq. (6)] was applied³¹ to estimate the full correlation energies and it is found that the changes in the reaction

enthalpies due to this extrapolation are very small, below $0.04 \text{ kcal mol}^{-1}$. Therefore, it can be concluded that the correlation energies calculated at the MP4 level of theory are well converged and that the contributions from the higher order terms are negligible.

The reaction enthalpies have been calculated for several commonly used basis sets of increasing size from 6-31G(d, p) to 6-311+G(3df, 2pd), plus Dunning's cc-pVTZ basis set, and these results are shown in Table IV. The calculated reaction enthalpies depend significantly on the basis set used. The quality of results improves in general with the size of basis set. Comparison of the influence of polarization versus diffuse functions on the reaction enthalpies indicates some interesting effects. The addition of polarization functions at the MP2 level of theory increases the calculated reaction enthalpy and improves the agreement with the experiment. The MP2 enthalpies calculated by basis sets supplemented with polarization and diffuse functions are even larger but they also overes-

TABLE V.

Decomposition of Calculated Reaction Enthalpies for α -Abstraction Reaction (R1) of Fluoroethane, Without Spin Projection Corrections, into Hartree–Fock and Correlated Contributions.^a

Basis set	ΔH_r^{HF}	$\Delta H_r^{(2)}$	$\Delta H_r^{(3)}$	$\Delta H_r^{(4)}$
6-31G(d, p)	-2.73	-13.21	4.75	-1.05
6-311G(d, p)	-3.54	-13.42	5.11	-1.75
6-311+G(d, p)	-5.18	-19.97	5.72	-2.18
6-311+G(2d, p)	-2.27	-14.66	6.18	-2.30
6-311G(2df, p)	-4.16	-14.34	5.34	-1.65

^a Results are in kilocalories per mole.

TABLE VI.

Calculated Barrier Heights and Reaction Enthalpies for α - (R1) and β -Abstraction (R2a and R2b) Reactions of Fluoroethane at Different Levels of Theory.^a

Basis set	$\Delta E_0^{(\text{MP2})}$			$\Delta E_0^{(\text{MP4})}$			$\Delta H_r^{(\text{MP2})}$		$\Delta E_0^{(\text{MP4})}$	
	R1	R2a	R2b	R1	R2a	R2b	R1	R2	R1	R2
6-31G(d, p)	1.85	2.14	0.85	2.95	3.48	2.35	1.77	3.24	5.49	6.75
6-311G(d, p)	0.80	0.50	-0.48	1.14	1.17	0.32	0.73	1.71	4.11	4.95
6-311+G(d, p)	1.12	0.32	0.18	1.38	0.84	0.84	-1.65	-1.52	1.92	1.87
6-311+G(2d, p)	0.80	0.05	-0.32	1.16	0.80	0.58	-1.83	-2.06	2.01	1.74
6-311G(2df, p)	-0.30	-0.44	-1.71	0.19	0.39	-0.73	-0.59	0.33	3.05	3.94
6-311+G(3df, 2p)	-0.06	-0.88	-1.11				-3.98	-3.64		
cc-pVTZ	-1.67	-2.19	-2.99				0.70	-1.70		
G2	1.95	4.34	3.26				-18.36	-14.87		

^a Values reported are differences between the MPn and G2 results. All energies are in kilocalories per mole. β abstraction has two possible pathways (R2a and R2b), via two rotamer transition-state structures.^{20, 21}

timate the experimental value by more than 1 kcal mol⁻¹. The 6-311+G(3df, 2p) basis set overestimates the reaction enthalpy at the MP2 level of theory by 3.6 kcal mol⁻¹. Thus, it will be of interest to test this large basis set with higher levels of perturbational approach. Unfortunately, due to our limited computational resources, we were not able to do this. For the MP3 and MP4 reaction enthalpies, addition of polarization and diffuse functions improves their agreement with the experiment.

COMPARISON OF MPn AND G2 RESULTS

The reaction enthalpies and barrier heights, calculated for the fluoroethane R1 and R2 reactions with hydroxyl radical, are compared with the results²⁰ obtained by the application of the G2 theory.²³ The aim of this comparative analysis is to find out which level of the Møller–Plesset perturbational approach is in the best agreement with the results of the G2 theory. The energies obtained from the G2 theory correspond effectively to the QCISD(T)/6-311 + G(3df, 2p) results. The G2 approach has also been shown²³ to reproduce experimental atomization and ionization energies with an average deviation of only 1.2 kcal mol⁻¹.

The barrier heights calculated at the G2 level of theory and the differences between the G2 barrier heights and the MP2 or MP4 results with different basis sets are given in Table VI. At the MP2 level of theory, the best agreement is obtained with the 6-311+G(2d, p) basis set, whereas for the MP4 results the smallest average deviation is obtained with the 6-311G(2df, p) basis set. In all cases devia-

tions are small, below 0.8 kcal mol⁻¹, but they are also unsystematic. The barrier heights are larger than the corresponding G2 values for reactions R1 and R2a, and smaller for the R2b reaction.

The reaction enthalpies calculated at the G2 level of theory and the differences between the G2 barrier heights and the MP2 or MP4 results with different basis sets are given in Table VI. The reaction enthalpies calculated at the MP2 level are in better agreement with the G2 results than the reaction enthalpies calculated at the MP4 level of theory, and the best agreement is obtained with the 6-311G(2df, p) basis set. For both reactions deviations are small, below 0.6 kcal mol⁻¹, but non-systematic. The MP2 reaction enthalpy is larger than the corresponding G2 value for the α abstraction (R1) and smaller for the β abstraction (R2).

The results obtained from the G2 formalism are in excellent agreement with the experimental data and they are superior to the barrier heights and the reaction enthalpies calculated at any level of the Møller–Plesset perturbational approach used in this study. Thus, it is clear that the G2 level of theory is the method of choice for calculating the reliable and accurate barrier heights and reaction enthalpies provided that necessary computational resources are available. If this is not computationally feasible or/and properties other than the reaction energetics are of interest, the best alternative seems to be the MP2 level of theory combined with the largest basis set that is computationally affordable. The basis set should be split valence of TZ quality and supplemented by diffuse and polarization functions. Such a combination of correlation method and basis set should ensure that the

quality of the calculated barrier heights and reaction enthalpies is within or close to chemical accuracy (± 1 kcal mol⁻¹) while keeping BSSE relatively small.

Conclusions

The convergence of reaction barriers and reaction enthalpies for the fluoroethane reactions with the hydroxyl radical, with respect to the size of the basis set and treatment of correlation energy, has been systematically investigated. Both the reaction barrier heights and reaction enthalpies are found to depend strongly on the size and the type of basis set used as well as on the level of correlation treatment applied. Results are in agreement with trends that have already been documented.^{4, 5, 12, 13}

The inclusion of correlation energy significantly decreases the calculated reaction barriers and increases the reaction enthalpies. Most correlation energy is already described by the MP2 term and it is well converged for both properties at the MP4 level of theory. The MP2 barrier heights and reaction enthalpies show the best agreement with the experimental data, whereas the MP3 results deviate the most from experiment.

The barrier heights and the reaction enthalpies have been calculated for several commonly used basis sets of increasing size from 6-31G(d,p) to 6-311+G(3df,2pd), including Dunning's cc-pVTZ basis set. The basis sets used were limited in size due to the limited computational resources but also due to our plans to extend the investigation to larger electronic systems, which are of interest in atmospheric chemistry. The quality of results improves in general with the size and flexibility of the basis set but it seems that the split valence basis sets of triple-zeta quality supplemented by diffuse and polarization functions are necessary to reproduce experimental values for the barrier heights and reaction enthalpies.

The basis set superposition errors (BSSEs) were estimated for the calculated barrier heights by the full counterpoise method. The BSSE values obtained at the correlated levels are significant quantities, from 2 to 5 kcal mol⁻¹. In general, the smallest barrier corrections are associated with those basis sets that contain polarization and diffuse functions. The most significant reduction of BSSE (ca. 2.5 kcal mol⁻¹) has been observed for the basis sets supplemented by diffuse functions. The augmentation of basis sets by polarization func-

tions is less effective in reducing BSSEs of the barrier heights (ca. 1 kcal mol⁻¹).

The uncorrected barrier heights are in better agreement with the experimental results than the counterpoise-corrected data. Similar results were obtained in several recent studies on hydrogen bonding in HF^{12e} and water^{12h, 34} dimers as well as for interaction energies^{12g} between helium or neon and methane. Thus, the usefulness of the full counterpoise corrections seems to be questionable and it should be used with caution. At the MP2 level of theory, which seems to be dictated for larger electronic systems of chemical interest, the optimal approach is to increase the basis set to the maximum size affordable and to use results from calculations without the counterpoise corrections.

The results obtained from the G2 scheme are in excellent agreement with the experimental data and they are superior to the barrier heights and the reaction enthalpies calculated at any level of the Møller–Plesset perturbational theory used in this study. In general, the G2 results were in the best agreement with the MP2 level of theory when the 6-311+G(2d,p) or 6-311G(2df,p) basis sets were used. Deviations were small, below 0.8 kcal mol⁻¹, but unfortunately they are also nonsystematic. For example, the barrier heights were larger than the corresponding G2 values for reactions R1 and R2a, and smaller for the R2b reaction. Thus, it is clear that the G2 level of theory is the method of choice for calculating reliable and accurate barrier heights and reaction enthalpies.

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